

Theory of Layered Iron Oxide on Frustrated Geometry: Electric Polarization, Magnetoelectric Effect and Orbital State

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A layered iron oxide $R\text{Fe}_2\text{O}_4$ (R : rare-earth elements) is an exotic dielectric material with charge-order (CO) driven electric polarization and magnetoelectric effect caused by spin-charge coupling. In this paper, a theory of electronic structure and dielectric property in $R\text{Fe}_2\text{O}_4$ is presented. Charge frustration in paired-triangular lattices allows a charge imbalance without inversion symmetry. Spin frustration induces reinforcement of this polar CO by a magnetic ordering. We also analyze an orbital model for the Fe ion which does not show a conventional long-range order.

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Ferroelectric (FE) material has a spontaneous electric polarization induced by displacement of ion and electronic cloud. A subtle balance of long-range Coulomb interaction, lattice potential and electron covalency derives the FE transition and controls the transition temperature. Recently revived magnetoelectric (ME) effects and related multiferroic phenomena [1, 2, 3] are recognized as spin-driven FE transitions. A key issue is a non-collinear spin structure in frustrated magnets where lattice displacement without inversion symmetry is induced by the symmetric and/or antisymmetric exchange strictions. Because of the observed gigantic ME effects, this type of materials has been examined from viewpoint of potential application as well as fundamental physics.

When electronic charges are ordered without inversion symmetry, a macroscopic electric polarization appears in a crystal. This can be another mechanism for ferroelectricity. This new class of ferroelectricity, which we call “electronic” ferroelectricity, is examined recently in the charge ordered manganites [4, 5] and several organic salts [6, 7]. Rare-earth iron oxides $R\text{Fe}_2\text{O}_4$ (R : rare-earth elements) [8] of the present interest belong to this class of materials. The crystal structure consists of paired Fe-O triangular lattices [Fig. 1(a)] and R-O block ones alternately stacked along the c axis. Since a nominal valence of Fe ion is 2.5+, an equal amount of Fe^{2+} and Fe^{3+} coexists in the paired triangular lattices. In the electron diffraction experiments, Bragg reflections at $(h/3 \ h/3 \ 3m+1/2)$ appear below 320K ($\equiv T_{\text{CO}}$) in LuFe_2O_4 . This observation indicates a valence order of Fe ion, i.e. a charge order (CO) of the Fe $3d$ electrons [9]. Around T_{CO} , a spontaneous electric polarization and dielectric anomalies turn up [10]. Moreover, around the ferrimagnetic spin ordering (SO) temperature ($T_{\text{SO}}=250\text{K}$) [11, 12], the gigantic ME effects are recently discovered [10, 13, 14].

These experiments imply that $R\text{Fe}_2\text{O}_4$ is not only a CO driven FE, but also a multiferroic material due to strong charge-spin coupling. A possibility of the ME effects in the “electronic” ferroelectrics ubiquitously exist in transition-metal oxides and organic salts. However, a guiding principle for searching the new class of multiferroic materials based on the electronic mechanism has not been fully examined until now. In this Letter, we present a theory of a dielectric mag-

net $R\text{Fe}_2\text{O}_4$ as a electronic ferroelectric and multiferroic material. We address the following issues: (i) origin of the electric polarization and the FE transition, (ii) mechanism of the coupling between electric polarization and magnetization, and (iii) orbital structure of the Fe ion. Present study shows that the novel dielectric properties in $R\text{Fe}_2\text{O}_4$ arise from interplay among the geometrical frustration and the multi-degrees of freedom of electron.

Start with the electronic structure in a single Fe ion in $R\text{Fe}_2\text{O}_4$. An Fe ion is five-fold coordinate with three O anions in the plane and two at apices [8]. We calculate the crystalline-field splitting for the $3d$ orbitals in a FeO_5 cluster based on the point-charge model. Split orbitals are assigned to the irreducible representation for the D_{3h} group: the $d_{3z^2-r^2}$ (A') orbital, and two sets of the doubly degenerate orbitals, $\{ad_{yz} - bd_{xy}, ad_{zx} + bd_{x^2-y^2}\}$ (E'') and $\{ad_{xy} + bd_{yz}, ad_{x^2-y^2} - bd_{zx}\}$ (E') where $a^2 + b^2 = 1$. The degenerate E' orbitals take the lowest energy with $a = 0.89$, although the energy levels for E' and E'' are close. Thus, each d orbital is singly occupied in Fe^{3+} ($S = 5/2$), and one of the lowest degenerate orbitals is doubly occupied in Fe^{2+} ($S = 2$), which has the orbital degree of freedom, as well as spin and charge [15]. This degree of freedom is treated by the pseudo-spin (PS) operator with amplitude of $1/2$: $\mathbf{T}_i = \frac{1}{2} \sum_{\xi, \xi', s} d_{i\xi s}^\dagger \sigma_{\xi\xi'} d_{i\xi' s}$ where $d_{i\xi s}$ is the electron annihilation operator with spin s and orbital ξ at site i , and σ are the Pauli matrices.

Now we set up the model Hamiltonian to describe the electronic structures and dielectric properties. The electrical resistivity in $R\text{Fe}_2\text{O}_4$ shows an insulating behavior even above T_{CO} [8]. This result implies that the $3d$ electrons are almost localized at Fe ions, and incoherent charge motion occurs by thermal hopping between Fe^{2+} and Fe^{3+} . In such insulating systems, the long-range Coulomb repulsion between charges, and the superexchange interaction between spins and orbitals play major roles on dielectric and magnetic properties. The Coulomb interaction Hamiltonian $\mathcal{H}_V = \sum_{(ij)} V_{ij} n_i n_j$ with the electron number n_i is mapped onto the Ising Hamiltonian $\mathcal{H}_V = \sum_{(ij)} V_{ij} Q_i^z Q_j^z$. Here, we introduce the PS operator Q_i^z for charge which takes $1/2$ ($-1/2$) for Fe^{3+} (Fe^{2+}). The superexchange interaction arises from the virtual electron hop-

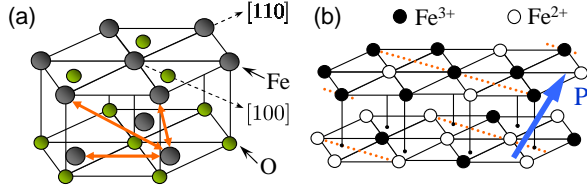


FIG. 1: (a): A pair of the Fe-O triangular lattices. Thick arrows represent the Coulomb interactions V_{abNN} , V_{cNN} and V_{cNNN} . (b): schematic view of $CO_{1/3}$ accompanied by the electric polarization

ping between Fe ions. The Hamiltonian is derived from the generalized pd model where the on-site Coulomb and exchange interactions for the Fe 3d and O 2p electrons and the electron hopping t_{pd} between the in-plane NN sites are introduced. Since the Coulomb interactions are larger than t_{pd} , the projection-perturbation theory up to $O(t_{pd}^4)$ is applied [1]. The high-spin states at Fe ions are chosen as initial states for the exchange processes, and all possible intermediate states are taken into account. The obtained Hamiltonian is classified by the valences of the NN Fe ions as $\mathcal{H}_J = \mathcal{H}_{22} + \mathcal{H}_{33} + \mathcal{H}_{23}$, where \mathcal{H}_{nm} is for the interaction between Fe^{n+} and Fe^{m+} . Each term includes the several exchange processes denoted by Γ as $\mathcal{H}_{nm} = \sum_{\Gamma} \mathcal{H}_{nm}^{(\Gamma)}$. We explicitly show one dominant term in \mathcal{H}_{22} ,

$$\begin{aligned} \mathcal{H}_{22}^{(1)} = & J_{22}^{(1)} \frac{1}{5} \sum_{\langle ij \rangle} \left(\frac{1}{2} \mathbf{I}_i \cdot \mathbf{I}_j + 3 \right) \left(\frac{1}{2} - 2\pi_i^l \pi_j^l \right) \\ & \times \left(\frac{1}{2} - Q_i^z \right) \left(\frac{1}{2} - Q_j^z \right). \end{aligned} \quad (1)$$

Here, \mathbf{I}_i is the spin operator with an amplitude of 2, and J_{22} is the exchange constant. We introduce the orbital PS operators π_i^l for the three-kinds of the in-plane nearest neighbor (NN) Fe-O bond directions, labeled by $l = (a, b, c)$. These are defined by $\pi_i^l = \cos(2\pi n_l/3) T_i^z + \sin(2\pi n_l/3) T_i^x$ with $(n_a, n_b, n_c) = (1, 2, 3)$. Details in \mathcal{H}_J will be presented elsewhere. It is clearly shown that spin \mathbf{I}_i , charge Q_i^z and orbital π_i^l degrees of freedom are coupled each other in \mathcal{H}_J . Among the several interactions, the inter-site Coulomb repulsion takes the largest energy scale. Thus, with lowering temperature (T), the charge sector will be frozen, at first. The expected spin ordering temperature is larger than that for the orbital because of the large magnitude of the spin operator, 2 and 5/2.

First we focus on origin of the CO transition accompanied by the electric polarization. We pay our attention to the polar CO state characterized by the momentum $\mathbf{q} = (1/3, 1/3, 0) \equiv \mathbf{q}_3$ [see in Fig. 1(b)]. As suggested by Yamada and coworkers [9], this CO, which we call $CO_{1/3}$, shows the electric polarization due to the charge imbalance between the triangular lattices. Along [110], charge alignments are schematically $\bullet \bullet \bullet \bullet \bullet$ in the upper layer, and $\circ \circ \circ \circ \circ$ in the lower one, where \circ (\bullet) represents Fe^{2+} (Fe^{3+}). This $CO_{1/3}$ competes with the non-polar CO with $\mathbf{q} = (1/2, 0, 0) \equiv \mathbf{q}_2$ ($CO_{1/2}$), and

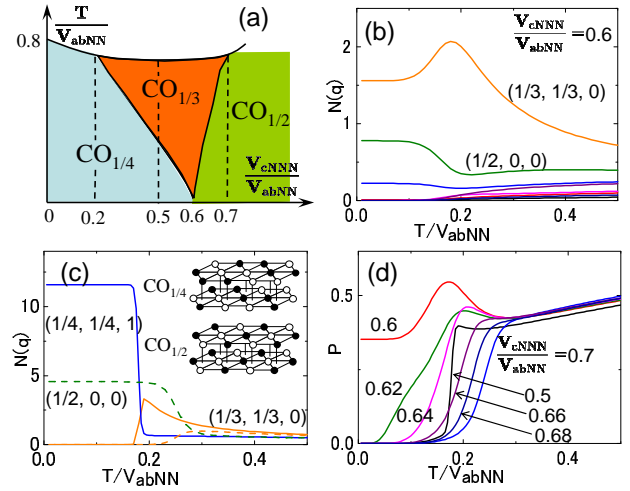


FIG. 2: (a): A mean-field phase diagram at finite T calculated in \mathcal{H}_V . (b): Charge correlation function $N(\mathbf{q})$ at $V_{cNNN}/V_{abNN} = 0.6$. (c): $N(\mathbf{q})$ at $V_{cNNN}/V_{abNN} = 0.5$ (bold lines) and 0.7 (broken lines). The insets show schematic views of the $CO_{1/4}$ and $CO_{1/2}$ structures. (d): Electric polarization P for several V_{cNNN}/V_{abNN} values. A value of V_{cNN}/V_{abNN} is chosen to be 1.2 in (a)-(d).

that with $(1/4, 1/4, 1) \equiv \mathbf{q}_4$ ($CO_{1/4}$) [see insets of Fig. 2(c)]. In both of $CO_{1/2}$ and $CO_{1/4}$, equal numbers of Fe^{2+} and Fe^{3+} exist in the lower and upper layers, and the electric polarization does not turn up.

To examine stability of the polar $CO_{1/3}$, we analyze \mathcal{H}_V in a pair of the triangular lattices, which is the minimal unit for the electric polarization. We introduce the largest three interactions V_{ij} [see Fig. 1(a)]: the inter-layer NN interaction (V_{cNN}), the intra-layer NN one (V_{abNN}) and the inter-layer next-nearest neighbor (NNN) one (V_{cNNN}). When the $1/r$ -type Coulomb interaction is assumed, we have $V_{cNN}/V_{abNN} = 1.2$ and $V_{cNNN}/V_{abNN} = 0.77$ for $LuFe_2O_4$. In the case of $V_{cNN} = V_{cNNN} = 0$, the above three CO's are the degenerate ground states (GS). Before going to precise calculations, we have performed the mean-field (MF) calculation to obtain a global phase diagram. At $T = 0$, $CO_{1/2}$ ($CO_{1/4}$) appears in the region of $2V_{cNNN} > V_{cNN}$ ($2V_{cNNN} < V_{cNN}$), and only on the phase boundary, $CO_{1/3}$ appears. At finite T [Fig. 2(a)], we have found that $CO_{1/3}$ is stabilized in a wide region between $CO_{1/2}$ and $CO_{1/4}$.

Unbiased calculations have been performed by utilizing the Monte Carlo (MC) simulation. A pair of the triangular lattices of $L \times L$ sites ($L = 6, 12$) with periodic-boundary condition is analyzed by the multi-canonical MC methods [17], where 8×10^6 MC steps are used for measurement. The resulting charge-correlation functions $N(\mathbf{q}) = L^{-2} \sum_{ij} \langle Q_i^z Q_j^z \rangle e^{i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)}$ [Figs. 2(b) and (c)] are qualitatively consistent with the MF phase diagram. At $V_{cNNN}/V_{abNN} = 0.6$ [Fig. 2(b)], $N(\mathbf{q}_3)$ shows a hump around $T/V_{abNN} = 0.18$ and keeps the largest value down to low T . On the other hand, at $V_{cNNN}/V_{abNN} = 0.5(0.7)$ [Fig. 2(c)], a dominant charge correlation function

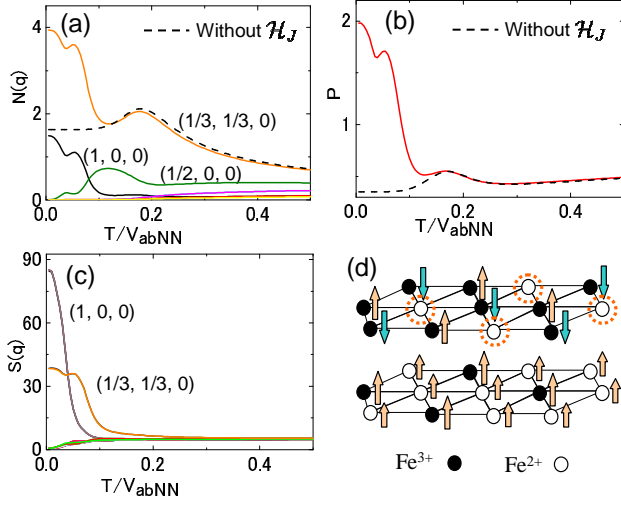


FIG. 3: Charge correlation function $N(\mathbf{q})$ (a), electric polarization P (b), and spin correlation function $S(\mathbf{q})$ (c) calculated in $\mathcal{H}_V + \mathcal{H}_J$. A schematic view of the charge and spin structure below the ferrimagnetic ordering temperature is shown in (d). Spin directions at the sites marked by broken circles are not uniquely determined.

changes from $N(\mathbf{q}_3)$ to $N(\mathbf{q}_2)$ [$N(\mathbf{q}_4)$] with decreasing T . This sequential phase transition may explain the experiments in $\text{YFe}_2\text{O}_{4-\delta}$; the observed superlattice spots in the electron diffraction change from $(n/3 \ n/3 \ 0)$ to $(n/4 \ n/4 \ 0)$ with decreasing T [18]. The spontaneous electric polarization is simulated by calculating $P = \langle p^2 \rangle^{1/2}$ [Fig.2(d)]. We define $p = L^{-1}(\sum_{i \in U} - \sum_{i \in L})Q_i^z$ where $\sum_{i \in U(L)}$ represents a summation of sites in the upper (lower) layer. At $V_{\text{cNNN}}/V_{\text{abNN}}=0.6$, a hump in P around $T/V_{\text{abNN}}=0.18$ corresponds to that in $N(\mathbf{q}_3)$ [19]. Apart from $V_{\text{cNNN}}/V_{\text{abNN}}=0.6$, a reduction of P is correlated with the increases of $N(\mathbf{q}_2)$ and $N(\mathbf{q}_4)$.

The stability of the polar $\text{CO}_{1/3}$ is caused by the charge frustration and an entropy gain on the paired-triangular lattices. Focus on the Fe sites located on the dotted lines in Fig. 1(b). The charge alignment at the Fe sites is responsible for the electric polarization. Since these sites are surrounded by three Fe^{2+} and three Fe^{3+} in the plane, the in-plane Coulomb interactions V_{abNN} are canceled out. Thus, the charge imbalance between the two layers occurs easily without loss of V_{abNN} , and the polar $\text{CO}_{1/3}$ is stabilized due to the inter-layer Coulomb interactions. At these Fe sites, large charge fluctuation remains at finite T and contributes to an entropy gain. This situation in $\text{CO}_{1/3}$ is in contrast to $\text{CO}_{1/2}$ and $\text{CO}_{1/4}$ where all sites are equivalent.

Now we examine coupling between the electric polarization and the magnetic ordering. The Hamiltonian $\mathcal{H}_V + \mathcal{H}_J$ is analyzed in a pair of the $L \times L$ triangular lattices by utilizing the multi-canonical MC method. The spin operators are set to be Ising spins, and the exchange constants are estimated by using the energy parameters for LaFeO_3 [20]. The orbital PS's in \mathcal{H}_J are set to be zero. This is reasonable, because the

expected SO temperature is much higher than that for orbital due to the large magnitudes of the spin operators. The resulting P , $N(\mathbf{q})$ and the spin correlation functions $S(\mathbf{q})$ are plotted in Fig. 3. Around $T/V_{\text{abNN}}=0.18$ in Fig. 3(a), $N(\mathbf{q}_3)$ shows a shoulder, corresponding to a hump in $N(\mathbf{q}_3)$ which is calculated without \mathcal{H}_J . Further increase in $N(\mathbf{q}_3)$ occurs around the spin ordering temperature $T/V_{\text{abNN}}=0.1$ [see Fig. 3(c)]. The temperature dependence of P [Fig. 3(b)] almost follows that of $N(\mathbf{q}_3)$. These results clearly show that the SO strongly stabilizes $\text{CO}_{1/3}$ accompanied by the electric polarization. The resulting SO is a ferrimagnetic structure characterized by the momentum \mathbf{q}_3 [Fig. 3(d)], which is consistent with the neutron diffraction experiments [11, 12].

The remarkable enhancement of the electric polarization below the SO temperature is caused by the spin-charge coupling and the spin frustration. Focus on the Fe^{2+} sites in the $2\text{Fe}^{3+}\text{-Fe}^{2+}$ (upper) layer in Fig. 3(d). Since these Fe ions are surrounded by the NN three-up and three-down spins of Fe^{3+} , spin directions at the sites are not determined uniquely. There is a large number of degenerate spin states, which contribute to an entropy gain. Because this spin structure is realized on the polar $\text{CO}_{1/3}$, this CO accompanied by the electric polarization is reinforced through the spin-charge coupling in \mathcal{H}_J . Essence of this mechanism is based on the spin frustration due to the antiferromagnetic configuration for the Fe^{3+} spins, and does not depend on detailed parameter choice. The present observation indicates a possibility of the large ME response [10, 13, 14]. By applying magnetic field in the CO/SO phase, melting of $\text{CO}_{1/3}$ and reduction of the electric polarization are expected.

Finally, we pay our attention to the orbital state. Until now, there are no experimental reports for the long-range orbital order and/or the Jahn-Teller lattice distortion in RFe_2O_4 . Thus, here we examine a possible orbital state in the CO/SO structure. By using the relation $\sum_l \pi_l^i = 0$, Hamiltonian \mathcal{H}_J is mapped onto an effective orbital model defined on the Fe^{2+} honeycomb lattice in the $2\text{Fe}^{2+}\text{-Fe}^{3+}$ layer [see Fig. 3(d)]. The model is easily derived as

$$\mathcal{H}_\tau = -J \sum_i \left(\tau_i^\alpha \tau_{i+\delta_\alpha}^\alpha + \tau_i^\beta \tau_{i+\delta_\beta}^\beta + \tau_i^\gamma \tau_{i+\delta_\gamma}^\gamma \right). \quad (2)$$

Here, δ_l indicates a NN Fe-Fe bond labeled by directions $l = (\alpha, \beta, \gamma)$ [see Fig. 4(a)], and $J(>0)$ is the exchange constant. We redefine the orbital PS operator as $\tau_i^l = \cos(\pi/2 + 2\pi n_l/3)T_i^z + \sin(\pi/2 + 2\pi n_l/3)T_i^x$ with $(n_\alpha, n_\beta, n_\gamma) = (0, 1, 2)$. This operator represents a projection of \mathbf{T}_i on the NN Fe-Fe bond direction. When (α, β, γ) is replaced by (x, y, z) in the Cartesian coordinate, this model corresponds to the e_g -orbital model on the cubic lattice [21, 22] which has been studied for KCuF_3 and LaMnO_3 . A related model is examined from the view point of the quantum computation [23]. It is worth noting that the interaction between orbitals explicitly depends on the bond direction. Although the honeycomb lattice is bipartite, there are intrinsic frustration effects; when PS's are arranged to gain bond energy for one direction, these are not fully favorable for other bonds.

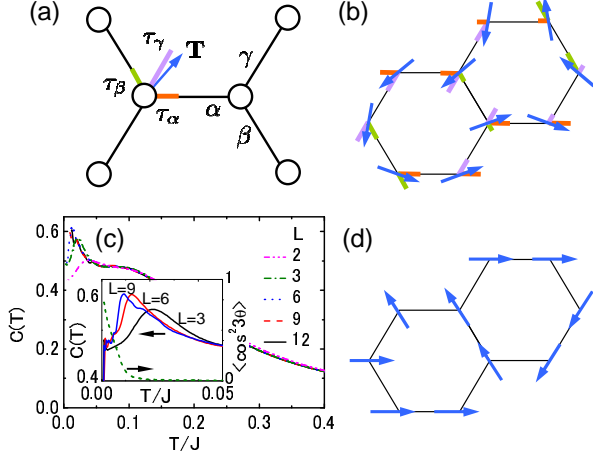


FIG. 4: (a): A schematic picture of the Fe^{2+} sublattice in the 2Fe^{2+} - Fe^{3+} layer. Bold arrows and bold bars represent the orbital PS direction and the PS projection components τ_i^l on the NN bonds, respectively. (b): One of the ground state PS configurations. (c): Specific heat $C(T)$ for several cluster sizes. Inset shows a magnification for a low T region. Broken line represents $\langle \cos^2 3\theta \rangle^{1/2}$ in $L=9$. (d): One of the PS configurations at finite temperature below T_0 .

This model provides a non-trivial orbital state. The Hamiltonian is rewritten as $\mathcal{H}_\tau = (J/2) \sum_{\langle ij \rangle} (\tau_i^l - \tau_j^l)^2 - J \sum_{il} (\tau_i^l)^2$, where the second term becomes a numerical constant. This form indicates a large number of the classical degenerate GS which satisfy $\tau_i^l = \tau_j^l$ for each NN ij pair. One of the PS configurations in the GS is shown in Fig. 4(b). The large degeneracy originates from the unusual orbital interaction. The momentum representation for the effective orbital interaction is given as $\mathcal{H}_\tau = \sum_{\mathbf{k}} \psi(\mathbf{k})^\dagger \hat{J}(\mathbf{k}) \psi(\mathbf{k})$ with a vector $\psi(\mathbf{k}) = [T_A^x(\mathbf{k}), T_A^z(\mathbf{k}), T_B^x(\mathbf{k}), T_B^z(\mathbf{k})]$ and a 4×4 matrix $\hat{J}(\mathbf{k})$. Here, A and B represent the two sublattices on the honeycomb lattice. Surprisingly, the lowest eigen-value for $\hat{J}(\mathbf{k})$ is a momentum-independent flat band at $-3J/4$. Thus, all eigen states with different \mathbf{k} provide the degenerate GS. At finite T , we analyze \mathcal{H}_τ on a $2 \times L \times L$ site cluster ($L = 2 \sim 12$) by using the multi-canonical MC method, where the PS operators are treated as classical vectors in the T^x - T^z plane. In the specific heat $C(T)$ [Fig. 4(c)], a peak appears around $T/J = 0.025$ for $L=3$. This characteristic temperature, denoted as T_0 , is much lower than the mean-field ordering temperature $3J/8$. The peak shifts to lower T and becomes sharp with increasing L . We also calculate the orbital correlation functions $\mathcal{T}^{lm}(\mathbf{q}) = L^{-2} \sum_{ij} e^{i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \langle T_i^l T_j^m \rangle$ ($l, m = x, z$) for all possible \mathbf{q} 's in clusters. However, the magnitudes are less than 20% of their maximum values, and remarkable increases in $\mathcal{T}^{lm}(\mathbf{q})$ are not observed with increasing L . To confirm a precise picture for the orbital state below T_0 in the thermodynamic limit, numerical calculations on larger sizes are required. However, within the present simulations, we have found a hidden parameter,

$\langle \cos^2 3\theta \rangle^{1/2} \equiv \langle [(2L^2)^{-1} \sum_i \cos 3\theta_i]^2 \rangle^{1/2}$, with the PS angle $\theta_i [\equiv \tan^{-1}(-T_i^z/T_i^x)]$. This parameter grows up below T_0 and approaches to 1 [see the inset of Fig. 4(c)]. This result implies that θ_i at each site takes one of the three angles $(2\pi n)/3$ with $n = (0, 1, 2)$, or one of the three $(2\pi n + \pi)/3$. One configuration is shown in Fig. 4(d) where $(2L^2)^{-1} \sum_i \cos 3\theta_i = +1$. At $T = 0$, any values for θ_i are allowed, as long as the relation $\tau_i^l = \tau_j^l$ is satisfied. Values of θ_i are fixed to be $(2\pi n)/3$ or $(2\pi n + \pi)/3$ by thermal fluctuations at finite T . This is the so-called order by fluctuation mechanism.

Summarizing, we present a theory of RFe_2O_4 as an exotic dielectric material with the CO driven electric polarization and the ME effects caused by the spin-charge coupling. The charge frustration allows the charge imbalance without inversion symmetry, i.e. the electric polarization. This CO is reinforced by the magnetic ordering where the spin frustration contributes to the entropy gain. The present mechanism of the ME effects is entirely different from the spin-lattice coupling mechanism proposed in the previous multiferroics, e.g. RMnO_3 . A possible orbital state is examined in the CO/SO. The effective orbital interaction does not depend on the momentum, indicating divergence of fluctuations. Instead of a conventional long-range order, a kind of the angle order of the pseudo spins grows up. The present study provides an insight for searching of a new class of "electronic" multiferroics in correlated electron systems.

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hump in P around $T/V_{\text{abNN}} = 0.18$ grows up, and a value of P around $T = 0$ reduces. This is because $\text{CO}_{1/3}$ degenerates with a number of non-polar CO with the momentum \mathbf{q}_3 at $T = 0$.

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